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Sub-T_g annealing effect on the kinetics of glass transition and crystallization for a Ti-Zr-Be-Fe bulk metallic glass

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ABSTRACT

The influence of sub-T_g pre-annealing on the kinetics of glass transition and crystallization of a lightweight $Ti_{41}Zr_{25}Be_{28}Fe_6$ bulk metallic glass (BMG) has been investigated by isochronal and isothermal differential scanning calorimetry tests. It was found that sub-T_g annealing obviously enlarges the supercooled liquid region of $Ti_{41}Zr_{25}Be_{28}Fe_6$ BMG, indicating an enhanced thermal stability. The activation energies for glass transition and crystallization of the as-cast and pre-annealed samples have been calculated and compared. The pre-annealed samples possess smaller values of fragility parameter and longer incubation times upon isothermal heating compared with the as-cast sample, indicating a retarded crystallization process. The isothermal crystallization kinetics of the samples with different annealed states has been investigated in terms of the Johnson-Mehl-Avrami equation and local Avrami exponent. The current study reveals a clear sub-T_g annealing effect on the kinetics of glass transition and crystallization of $Ti_{41}Zr_{25}Be_{28}Fe_6$ glassy alloy and the possible mechanisms have also been proposed.

1. Introduction

Bulk metallic glasses (BMGs) are a class of advanced materials with wide application aspects [1,2]. However, because of the metastable nature, structural changes such as crystallization [3,4] and structural relaxation [5,6] may occur under certain conditions such as annealing [7], stress [8] and irradiation [9], leading to the changes in mechanical and physical properties [10–12]. Be different from crystallization, structural relaxation induces only local atomic rearrangement which lowers the free energy of BMGs but the amorphous structure is still maintained. Low temperature (sub-T_g, here T_g is the onset glass transition temperature) annealing treatment is one of the most widely used methods to induce structural relaxation of BMGs [6,7,13–16]. As thermal history may affect the glass transition and crystallization behavior of BMGs, it is meaningful to investigate the kinetics of glass transition and crystallization of BMG samples with different annealed state, which may also provide useful information for understanding the effects of structural relaxation on the subsequent glass transition and crystallization. Till now, the effects of sub-T_g annealing on the kinetics of glass transition and crystallization of some Zr-based [7,13] and Cu-based MGs [6] have been studied. In order to fully understand the relationship between structure relaxation and the following glass transition and crystallization, it is still necessary to conduct the research based on other typical BMGs.

Ti-based BMGs are very attractive among the developed BMGs because of their unique properties such as high specific strength, good corrosion resistance [17]. In our previous works, we developed a series of lightweight Ti-based BMGs with improved glass-forming ability (GFA) and mechanical properties by alloying technique [18]. The effects of alloying elements (e.g. Fe, Al, Ag, Cu, Ni, V and Cr) on crystallization kinetics of a $Ti_{41}Zr_{25}Be_{34}$ BMG has also been investigated systematically [19,20]. It has been found that the Fe-containing alloy exhibits quite different crystallization behavior from other alloys, implying a more complex atomic configuration. In this study, we mainly focus on the effect of sub-T_g annealing on the kinetics of glass transition and crystallization of the magic $Ti_{41}Zr_{25}Be_{28}Fe_6$ BMG. For comparison with those of the as-cast sample, the kinetics of glass transition and crystallization of $Ti_{41}Zr_{25}Be_{28}Fe_6$ alloy samples at different pre-annealed conditions has been investigated by differential scanning calorimetry (DSC). The relationship of glass transition and crystallization with structural relaxation has also been explored.

2. Experimental procedure

The ingots with composition of $Ti_{41}Zr_{25}Be_{28}Fe_6$ were prepared by arc melting the mixture of high purity elements (> 99.99%) under a Ti-

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gettered high-purity argon atmosphere. Each ingot was remelted for at least four times to ensure chemical homogeneity. Then as-cast rods with a diameter of 3 mm and a length of 55 mm were prepared by copper mould suction casting method. Slices with a thickness of 2 mm were cut from the as-cast rods to prepare the pre-annealed samples. The slices were sealed in vacuum quartz tubes under vacuum (1×10^{-2} Pa) and annealed in a preheated resistance furnace (the temperature accuracy: ± 5 °C) at 563 K and 578 K for 40 min. Then the quartz tubes were taken out from the furnace and cooled in air to the room temperature. After annealing, the oxide layers on the surface of the samples were removed by mechanical polishing. The structure of the as-cast and pre-annealed $Ti_{41}Zr_{25}Be_{28}Fe_6$ samples was examined by X-ray diffraction (XRD, Rigaku D/max-RB with Cu Kα radiation) and transmission electron microscopy (TEM, FEI Tecnai G20, 200 kV). The thin foil specimens for TEM observation were prepared by a standard twin-jet electrochemical polishing with a solution of 8%$HClO_4$ and 92% C_2H_5OH at − 15 °C cooled by liquid nitrogen. Thermal properties were characterized using a NETZSCH STA 409C/CD DSC under the protection of high purity Ar gas flow at heating rates ranging from 5 to 40 K/min. To study the isothermal crystallization kinetics, the as-cast and pre-annealed samples were put in DSC (Perkin Elmer Instruments, PYPI diamond), heated to the selected temperature at a fast heating rate of 150 K/min and then held for a certain period until the crystallization was completed. The indium and zinc standards were used for the temperature and enthalpy calibration of the DSC systems, giving an accuracy of ± 0.5 K and ± 0.1 mW, respectively. The hardness tests were conducted using a Hysitron TI 750 Ubi nanoindenter at a maximum load of 10 mN and a loading rate of 2 mN/s. At least eight tests were conducted under each condition to get the average values of hardness. The density of as-cast and pre-annealed samples was measured by Archimides method with the help of an analytical electronic balance (Sartorius BSA124S-CW, accuracy: ± 0.1 mg).

3. Results and discussion

3.1. Non-isothermal crystallization kinetics

According to our previous study [19,20], the T_g value of as-cast $Ti_{41}Zr_{25}Be_{28}Fe_6$ glassy alloy is 600.3 K (heating rate: 20 K/min). In this study, the as-cast $Ti_{41}Zr_{25}Be_{28}Fe_6$ samples were pre-annealed at 563 K and 578 K for 40 min, respectively. Fig. 1a shows the XRD patterns of the as-cast and pre-annealed $Ti_{41}Zr_{25}Be_{28}Fe_6$ samples. No perceptible crystalline phases have been detected for all the three samples. However, it was also found that the 2θ value corresponding to the maximum intensity of the broad peak (labeled as $2\theta_{max}$), increases slightly after annealing. By Gauss fitting, the values of $2\theta_{max}$ of the as-cast, 563 K-annealed and 578 K annealed samples have been determined as 38.079°, 38.247° and 38.250° (as shown in Fig. 1b), respectively. With the increase of annealing temperature, the $2\theta_{max}$ value also increases, indicating that the distance between the adjacent atoms in the clusters decreases, which relates with the structural relaxation [21]. Fig. 2a–c display bright-field TEM images and the corresponding selected area electron diffraction patterns for the as-cast, 563 K annealed and 578 K annealed samples, which also verifies the amorphous structure.

Fig. 3 displays the continuous DSC curves of as-cast and pre-annealed $Ti_{41}Zr_{25}Be_{28}Fe_6$ samples at different heating rates. All the DSC traces exhibit a clear glass transition followed by two exothermic crystallization peaks. The characteristic temperatures (e.g. the onset glass transition temperature T_g, the onset crystallization temperature T_x, and the peak temperatures T_{p1} and T_{p2}) and supercooled liquid region (ΔT_x, defined as T_x-T_g) were determined and their values are listed in Table 1. For all the three samples, it can be seen that the characteristic temperatures shift to higher temperature with the increase of heating rate, implying the glass transition and crystallization of the samples are rate dependent. Similar phenomena have been observed in other BMGs [22–27]. It is also noticed that after annealing, T_x, T_{p1} and

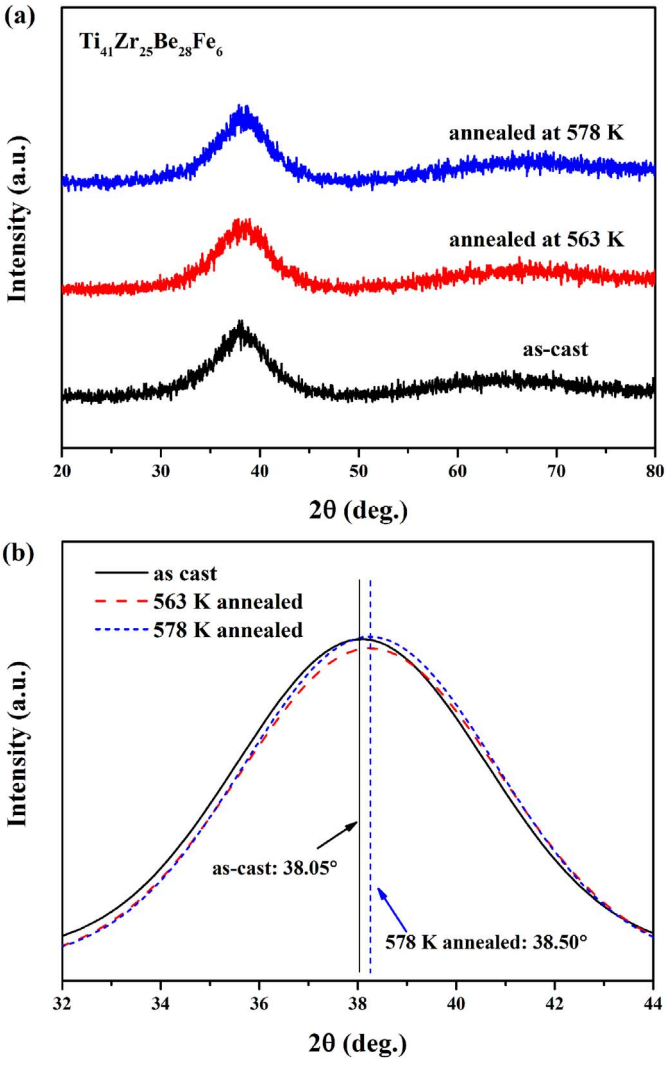

Fig. 1. (a) XRD patterns for the as-cast and pre-annealed $Ti_{41}Zr_{25}Be_{28}Fe_6$ alloy samples. (b) The Gauss fittings of XRD curves.

T_{p2} increases while T_g decreases more obviously. The T_g values of 563 K annealed and 578 K annealed samples are 585.4 K and 594.6 K respectively (heating rate: 20 K/min), which are 14.9 K and 5.7 K lower than that of the as-cast sample. As a result, the pre-annealed samples show a wider supercooled liquid region compared with that of the as-cast sample, indicating the enhancement of thermal stability. Especially the ΔT_x value of 563 K annealed sample is 141.3 K (heating rate: 20 K/min), which is enhanced by 15.2%. The difference between the values of crystallization enthalpy for different samples is < 1 J/g, which further confirms the amorphous structure of the pre-annealed samples

In order to get more details, the DSC curves of the as-cast and pre-annealed $Ti_{41}Zr_{25}Be_{28}Fe_6$ samples have been compared emphatically in the temperature range near T_g (heating rate: 20 K/min). As shown in Fig. 4, for the as-cast sample, a broad pre-exothermic event is seen before the main endothermic as well as exothermic events. In the case of pre-annealed samples, the pre-exothermic event is almost absent. It is already known that the heat release of the exothermic reaction occurred below T_g is due to structural relaxation [28,29]. In this sense, the sub-T_g annealing results in a substantial reduction in the free volume content. Accordingly, the structural relaxation enthalpy dramatically decreases from 10.4 J/g for the as-cast sample to almost 0 for the annealed samples. The pre-annealed samples also possess relatively higher density. The densities of 563 K annealed and 578 K annealed samples are 4.895 ± 0.001 g/cm^3 and 4.897 ± 0.001 g/cm^3, respectively, which